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(54) Title: FUEL LUBRICITY ADDITIVES (57) Abstract There is disclosed a fuel lubricity additive, made by a two-step process wherein the first step is co-reacting an unsaturated base oil, predominantly from vegetable oil sources, and a compound having a diene structure and a carboxylic acid group, wherein the second step is esterifying or amidifying the free carboxylic acid group of anhydride group with a polyhydroxy-containing compound or polyamine compound to form the final fuel lubricity additive useful in diesel fuels. The inventive fuel lubricity additive also is useful as a dispersant.		

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FUEL LUBRICITY ADDITIVES

Technical Field of the Invention

5 The present invention provides a fuel lubricity additive, made by a two-step process wherein the first step is co-reacting an unsaturated base oil, predominantly from vegetable oil sources, and a compound having a diene structure and a carboxylic acid group, wherein the second step is esterifying or amidafying the free carboxylic acid group or groups with a poly-
10 hydroxy-containing compound or poly-amine compound to form the final fuel lubricity additive useful in diesel fuels. The fuel lubricity additive formulations and compositions have further utility as dispersants.

Background of the Invention

15 Beginning in 1993, all highway diesel fuel in the United States was required to have a minimum sulfur content of 0.05% (by weight). Refineries have been able to meet this standard by hydrotreating. Hydrotreating removes sulfur, nitrogen and other metal-bonding reactive sites as well as seal-swelling and lubricating aromatic compounds. However, a major drawback to the hydrotreating process used to reduce sulfur and aromatic levels is that the diesel fuel product has reduced fuel lubricity. The reduced fuel lubricity increases wear rates
20 in many fuel injection systems, as such injections systems have been designed to utilize natural lubricating properties of traditional diesel fuels (typically containing 0.2 to 0.5% by weight sulfur or 2000-5000 ppm). This has caused a dramatic increase in fuel injection system problems manifest as underrun and stalling as the most minor to injector nozzle fouling, to fuel pump failures resulting in a need to replace entire systems. This is causing fuel injection
25 systems to be redesigned even as injection pressures have risen to the detriment of wear and mechanical performance.

 Distillate petroleum hydrocarbon fractions in the kerosene/diesel fuel range have essentially no lubricity or lubricating value. The high solvent action of the fuel and the constant washing by large volumes of fuel make it impossible to maintain lubricant on pump
30 surfaces. Thus, fuel pumps are subjected to serious wear, leading to pump failure. Fuel compositions have to be treated (formulated) to address wear, erosion and corrosion problems.

 Petroleum refineries produce 50 to 60 billion gallons of diesel fuel for consumption in the United States each year. Most refineries are producing only low-sulfur diesel fuels to achieve economies of scale. This means that, even though off-road vehicles are currently
35 exempt from the low-sulfur emission requirements, most, including tractor and other farm equipment, will be using low-sulfur diesel fuels. This will result in increased engine wear in agricultural equipment that was designed for the natural lubricating properties of diesel fuels. The EPA is in the process of developing emission standards for off-road engines that will also cause low-sulfur diesel fuels to be used.

Traditional fuel lubricity additives contain sulfur, phosphorous, zinc, nitrogen or boron. These are called ash forming or catalyst-poisoning additives. Ash forming additives are thermally activated and form sacrificial chemical bonds to metal surfaces. The additives will then "shear" from the metal surface before the metal itself, resulting in protection of the metal surface from wear. Many additives also contribute to particulate emissions during combustion. Moreover, additives can form SO_x , NO_x and PO_x emissions, or emissions which can poison a catalyst used in catalytic converters, causing an increase in particulate and hydrocarbon emissions.

Therefore there is a need in the art for diesel fuel additives that impart needed lubricity properties but provide minimal ash or preferably ash-less properties for the purposes of reducing ultimate emissions characteristics. The present invention applies telomer technology to this field of art to provide an improved ashless additive to diesel fuel and kerosene that provides lubricity properties, improved combustion and improved emissions characteristics. The goal, that was achieved by this invention, was to provide a fully fuel-soluble additive molecule, which is derived from renewable sources and contains no ash or deposit-producing elements or catalyst poisons such as sulfur, phosphorous or boron. The invention describes the achievement of that goal.

Summary of the Invention

The present invention provides a fuel lubricity additive compound, comprising an intermediate adduct of a first moiety reacted in a first reaction with a second moiety to form the intermediate adduct and further esterifying or amidafying the intermediate adduct with a third moiety in a molar ratio of from about 1:2 to about 2:1, wherein the first moiety is an unsaturated triglyceride plant oil or a thermal polymer thereof, wherein the second moiety is a diene or conjugated carbon-carbon double bond acid or anhydride moiety, wherein the first reaction comprises mixing the first moiety with the second moiety in a molar ratio of from about 1:2 to about 2:1 at a temperature of from about 130 °C to about 195 °C under an inert atmosphere; and wherein the third moiety is a polyhydroxy compound or a polyamino compound. Preferably, the unsaturated plant oil is selected from the group consisting of rapeseed oil, tung oil, linseed oil, soya oil, corn oil, peanut oil, canola oil, safflower oil, or combinations thereof. Preferably, the thermal polymer is selected from the group consisting of thermal (telomer) polymers of canola oil, soya oil, linseed oil, corn oil, safflower oil, peanut oil, tung oil, and combinations thereof. Preferably, the second moiety comprises unsaturated compounds having a free carboxylic acid or anhydride group. Most preferably, the second moiety is selected from the group consisting of maleic acid, maleic anhydride, sorbic acid, sorbic anhydride, tetrahydrophthalic anhydride, tetrahydrophthalic acid, salicylic acid, salicylic anhydride, acrylic acid, acrylic anhydride, C_{1-10} alkyl, C_{2-10} alkenyl, or C_{1-10} alkoxy derivatives of the foregoing acids and anhydrides, and combinations thereof. Preferably, the polyhydroxy compound of the third moiety is selected from the group consisting of glycerol, sorbitol,

hydroxyquinone, glucose, mannose, 6-carbon sugars, pentose, fructose, 5-carbon sugars, pentaerythritol, catechol, resorcinol, hydroquinone, pyrogallol, 4,4'-dihydroxybiphenyl, 2,4-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, orthohydroxybenzene, polyhydroxyaromatic compounds having one or two phenyl rings and one or two 5-6 membered aromatic rings
5 having substituted alkyl or alkenyl side chains (C₂₋₁₀) substituted with at least two hydroxyl groups, trimethylolpropane, pentaerythritol, dimethylolpropane, dipentaerythritol, trimethylolethane, ethyleneglycol, polypropyleneglycol, polyethylated alcohols, and combinations thereof. Preferably, the polyamino compound is selected from the group consisting of diethylenetriamine, dimethylenetriamine, dipropylnetriamine, ethylenediamine,
10 propylenediamine, butylenediamine, butylenetriamine, triethylenetetramine, tripropylenetetramine, trimethylenetriamine, tributylenetetramine, tetraethylenepentamine, tetramethylenepentamine, tetrapropylenepentamine, tetraethylenepentamine, tetrabutylenepentamine, hexylenediamine, and combinations thereof. Preferably, the first reaction is conducted under continuous mixing. Preferably, the esterification reaction
15 comprises reaction conditions of from about 150 °C to about 190 °C under an inert atmosphere and further comprises adding an esterification catalyst. Most preferably, the esterification catalyst is an acid catalyst. Most preferably, the esterification catalyst is selected from the group consisting of p-toluene sulfonic acid, hydrophosphorous acid, sulfuric acid, hydrochloric acid, phosphoric acid, acid-activated clays, solid acid catalysts, acidic zeolites, and
20 combinations thereof. Preferably, the amidification reaction comprises reaction conditions of from about 130 °C to about 150 °C under an inert atmosphere. Most preferably, the fuel lubricity additive compound is made from the first moiety, second moiety and third moiety compounds selected from the group consisting of in order soya oil-maleic anhydride-sorbitol, soya oil-linseed oil combination-maleic anhydride-sorbitol, soya oil-maleic anhydride-
25 ethylenediamine, and soya oil-maleic anhydride-hydroquinone.

The present invention further provides a process for synthesizing a fuel lubricity additive compound, comprising

(a) reacting an unsaturated triglyceride plant oil or a thermal polymer thereof first moiety with a second moiety in a molar ratio of from about 1:2 to about 2:1 at a temperature of
30 from about 130 °C to about 195 °C under an inert atmosphere to form an intermediate adduct, wherein the second moiety is a diene or conjugated carbon-carbon double bond acid or anhydride moiety; and

(b) esterifying or amidifying the intermediate adduct with a third moiety in a molar ratio of from about 1:2 to about 2:1, wherein the third moiety is a polyhydroxy compound or a
35 polyamino compound.

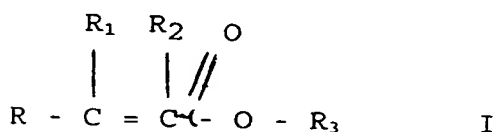
Preferably, the unsaturated plant oil is selected from the group consisting of rapeseed oil, tung oil, linseed oil, soya oil, corn oil, peanut oil, canola oil, safflower oil, or combinations thereof. Preferably, the thermal polymer is selected from the group consisting of thermal (telomer) polymers of canola oil, soya oil, linseed oil, corn oil, safflower oil, peanut oil, tung

oil, and combinations thereof. Preferably, the second moiety comprises unsaturated compounds having a free carboxylic acid or anhydride group. Most preferably, the second moiety is selected from the group consisting of maleic acid, maleic anhydride, sorbic acid, sorbic anhydride, tetrahydrophthalic anhydride, tetrahydrophthalic acid, salicylic acid, salicylic anhydride, acrylic acid, acrylic anhydride, C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, or C₁₋₁₀ alkoxy derivatives of the foregoing acids and anhydrides, and combinations thereof. Preferably, the polyhydroxy compound of the third moiety is selected from the group consisting of glycerol, sorbitol, hydroxyquinone, glucose, mannose, 6-carbon sugars, pentose, fructose, 5-carbon sugars, pentaerythritol, catechol, resorcinol, hydroquinone, pyrogallol, 4,4'-dihydroxybiphenyl, 2,4-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, orthohydroxybenzene, polyhydroxyaromatic compounds having one or two phenyl rings and one or two 5-6 membered aromatic rings having substituted alkyl or alkenyl side chains (C₂₋₁₀) substituted with at least two hydroxyl groups, trimethylolpropane, pentaerythritol, dimethylolpropane, dipentaerythritol, trimethylolethane, ethyleneglycol, polypropyleneglycol, polyethylated alcohols, and combinations thereof. Preferably, the polyamino compound is selected from the group consisting of diethylenetriamine, dimethylenetriamine, dipropylnetriamine, ethylenediamine, propylenediamine, butylenediamine, butylenetriamine, triethylenetetramine, tripropylenetetramine, trimethylenetriamine, tributylenetetramine, tetraethylenepentamine, tetramethylenepentamine, tetrapropylenepentamine, tetraethylenepentamine, tetrabutylene-pentamine, hexylenediamine, and combinations thereof. Preferably, the first reaction is conducted under continuous mixing. Preferably, the esterification reaction comprises reaction conditions of from about 150 °C to about 190 °C under an inert atmosphere and further comprises adding an esterification catalyst. Most preferably, the esterification catalyst is an acid catalyst. Most preferably, the esterification catalyst is selected from the group consisting of p-toluene sulfonic acid, hydrophosphorous acid, sulfuric acid, hydrochloric acid, phosphoric acid, acid-activated clays, solid acid catalysts, acidic zeolites, and combinations thereof. Preferably, the amidification reaction comprises reaction conditions of from about 130 °C to about 150 °C under an inert atmosphere.

The present invention provides a diesel fuel composition having a fuel lubricity additive compound, comprising a diesel fuel and from about 50 ppm to about 5000 ppm of a fuel lubricity additive, wherein the fuel lubricity additive comprises an intermediate adduct of a first moiety reacted in a first reaction with a second moiety to form the intermediate adduct and further esterifying or amidifying the intermediate adduct with a third moiety in a molar ratio of from about 1:2 to about 2:1, wherein the first moiety is a unsaturated triglyceride plant oil or a telomerized polymer thereof, wherein the second moiety is a diene or conjugated carbon-carbon double bond acid or anhydride moiety, wherein the first reaction comprises mixing the first moiety with the second moiety in a molar ratio of from about 1:2 to about 2:1 at a temperature of from about 130 °C to about 195 °C under an inert atmosphere; and wherein the third moiety is a polyhydroxy compound. Preferably, the unsaturated plant oil is selected from

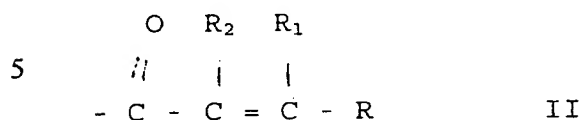
- the group consisting of rapeseed oil, tung oil, linseed oil, soya oil, corn oil, peanut oil, canola oil, safflower oil, or combinations thereof. Preferably, the thermal polymer is selected from the group consisting of thermal (telomer) polymers of canola oil, soya oil, linseed oil, corn oil, safflower oil, peanut oil, tung oil, and combinations thereof. Preferably, the second moiety
- 5 comprises unsaturated compounds having a free carboxylic acid or anhydride group. Most preferably, the second moiety is selected from the group consisting of maleic acid, maleic anhydride, sorbic acid, sorbic anhydride, tetrahydrophthalic anhydride, tetrahydrophthalic acid, salicylic acid, salicylic anhydride, acrylic acid, acrylic anhydride, C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, or C₁₋₁₀ alkoxy derivatives of the foregoing acids and anhydrides, and combinations thereof.
- 10 Preferably, the polyhydroxy compound of the third moiety is selected from the group consisting of glycerol, sorbitol, hydroxyquinone, glucose, mannose, 6-carbon sugars, pentose, fructose, 5-carbon sugars, pentaerythritol, orthohydroxybenzene, polyhydroxyaromatic compounds having one or two phenyl rings and at least two hydroxyl groups (*e.g.*, having a phenyl moiety substituted in any of the foregoing polyhydroxy compounds),
- 15 trimethylolpropane, polyethoxylated alcohols, and combinations thereof. Preferably, the polyamino compound is selected from the group consisting of diethylenetriamine, dimethylenetriamine, dipropylnetriamine, ethylenediamine, propylenediamine, butylenediamine, butylenetriamine, triethylenetetramine, tripropylenetetramine, trimethylenetriamine, tributylenetetramine, tetraethylenepentamine, tetramethylenepentamine, tetrapropylenepentamine, tetraethylenepentamine, tetrabutylenepentamine, hexylenediamine, and combinations thereof. Preferably, the first reaction is conducted under continuous mixing. Preferably, the esterification reaction comprises reaction conditions of from about 150 °C to about 190 °C under an inert atmosphere and further comprises adding an esterification catalyst. Most preferably, the esterification catalyst is an acid catalyst. Most preferably, the
- 25 esterification catalyst is selected from the group consisting of *p*-toluene sulfonic acid, hydrophosphorous acid, sulfuric acid, hydrochloric acid, phosphoric acid, acid-activated clays, solid acid catalysts, acidic zeolites, and combinations thereof. Most preferably, the fuel lubricity additive compound is made from the first moiety, second moiety and third moiety compounds selected from the group consisting of in order soya oil-maleic anhydride-sorbitol, soya oil-linseed oil combination-maleic anhydride-sorbitol, soya oil-maleic anhydride-ethylenediamine, and soya oil-maleic anhydride-hydroquinone.
- 30

A fuel lubricity additive or a dispersant comprising the product of a first and a second reaction, (a) wherein the first reaction is an addition reaction of a base oil and a dienophile having a carboxylic acid moiety selected from a formula I or a formula III:

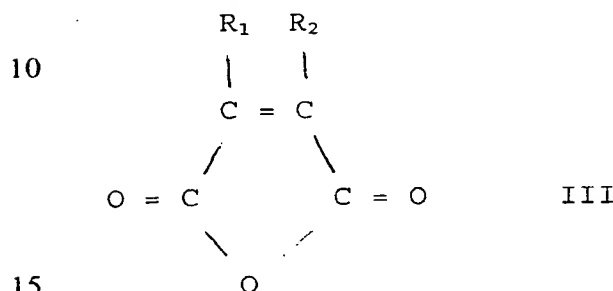


wherein R, R₁ and R₂ are independently hydrogen, hydroxyl, a straight chain or branched chain

C₁₋₁₂ alkyl, C₁₋₁₂ acyl, C₁₋₁₂ aryl, C₄₋₁₂ cycloalkyl, or C₁₋₁₂ alkoxy; and wherein R₃ is hydrogen, a straight chain or branched chain C₁₋₁₂ alkyl, C₁₋₁₂ acyl, C₁₋₁₂ aryl, C₄₋₁₂ cycloalkyl, or C₁₋₁₂ alkoxy, or formula II



or formula III



wherein R₁ and R₂ are the same as in formula I; and

- (b) wherein the second reaction is an esterifying or an amidafying of the carboxylic acid functional moiety of the aliphatic intermediate product of the first reaction with a polyol compound or polyamino compound having from 2 to 10 free hydroxyl groups and selected from the group consisting of substituted or unsubstituted mono-, di-, tri-, tetra- or penta-sugars, glycerols, glycols, pentaerythrols, and combinations thereof, wherein the substitutions are selected from the group consisting of hydroxyl, oxo, halogen (chloro, bromo, iodo, fluoro), straight chain or branched chain C₁₋₁₂ alkyl, C₁₋₁₂ acyl, C₁₋₁₂ aryl, C₄₋₁₂ cycloalkyl, hydroxyl, and C₁₋₁₂ alkoxy. Preferably, the dienoid carboxylic acid is selected from the group consisting of maleic acid, sorbic acid, acrylic acid, and combinations thereof. Preferably, the base oil is selected from the group consisting of HEAR (high erucic acid rapeseed oil), linseed oil, soybean oil, canola oil, telomer oil having a kinematic viscosity of 6000 SUS, and combinations thereof. Preferably, wherein the base oil is either a triglyceride (all straight chain) with at least one of the acyl chains being unsaturated, or a straight chain wax ester of from about 18-48 carbons atoms in length and being at least monounsaturated. Most preferably, the base oil acyl fatty acid chains of the triglyceride are from 3 to 24 carbon atoms in length (straight) and have from one to three double bonds. Most preferably, the base oil unsaturated fatty acid acyl chains have from 10-24 carbons atoms.

35 **Brief Description of the Figures**

Figure 1 shows a chemical structure of the product of a reaction between an unsaturated fatty acid and a dienoid adduct and then further esterification or amidification. Specifically, the structure shown in Figure 1 is the reaction product, according to the present invention, of HEAR (high erucic acid rapeseed oil), maleic anhydride and trimethylolpropane.

Figure 2 shows the results of a 4 ball wear test of rapeseed oil as the base oil, maleic anhydride or sorbic acid as a carboxylic acid-containing adduct and sorbitol or glycerine as the esterified polyol. These data shown are for low viscosity polyalphaolefin (POA, a synthetic paraffinic oil with no sulfur), which can serve as an extreme model of hydrotreated diesel oil. Moreover, addition of the inventive additive (5% by weight) provided significant antiwear properties to PAO as measured by decreased wear scar size.

Figure 3A shows improvement in SLBOCLE loads with increasing concentrations of HEAR-sorbic acid-sorbitol and soy oil-sorbic acid-sorbitol additives at the concentrations noted. Figure 3B shows improvement in HFRR scars with increasing concentration of the same additives.

Detailed Description of the Invention

Synthetic Process

The synthetic process for the production of the inventive dispersants or fuel lubricity additives is a two-step process. The first step reacts the triglyceride with a dieneophile in a Diels-Alder reaction. This first step is an adduction reaction accomplished by reacting an unsaturated site of an unsaturated triglyceride oil, such as HEAR, with a dieneophile having conjugation of the double bonds and carboxylic acid group. Examples of the dieneoids are maleic anhydride, acrylic acid, sorbic acid, and ascorbic acid (vitamin C). All of the adducts are characterized by having a conjugated double bond moiety that is not sterically hindered for the Diels-Alder reaction and a free carboxylic acid moiety available for reaction in the second process step.

The Diels-Alder reaction is initiated, for example, by mixing the unsaturated triglyceride and the dieneophile on a 1:1 molar basis and adding a small amount (0.5% to 5% by weight of the dienophile) of di-t-butylperoxide and heat (range of 120 °C to 180 °C). The Diels Alder reaction proceeded until there was no further evolution of vapor phase of water, butanol (from the catalyst di-t-butylperoxide) and unreacted adduct component. The results of the first reaction step using HEAR as the unsaturated triglyceride and either styrene, maleic anhydride, acrylic acid or sorbic acid at various molar ratios is provided in Table 1.

Table 1

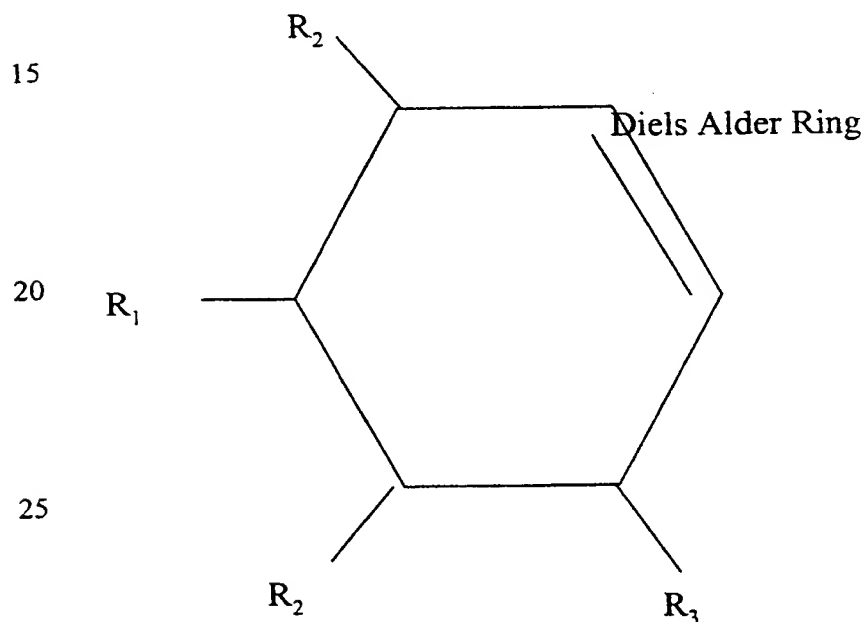
dieneophile	molar ratio copolymer:H EAR	exotherm, max delta, °C	acid number	iodine number	% complete (calculated)
maleic anhydride	0.5:1	9	24.6	74.7	100
maleic anhydride	1:1	24	65.9	58.7	85
acrylic acid	1:1	liquid addition	100	66.3	100

sorbic acid 1:1 <5 32.0 95.0 62

The second step reacts the carboxylic acid moiety on an aliphatic ring intermediate with either a polyol or polyamine polar reactant (in a esterification or amidification reaction, depending upon the reactant) to form final products that are dispersants or diesel fuel lubricity additives. Illustrative polyols include glycerol (three hydroxyl groups) and the sugar derivative sorbitol with six chiral hydroxyl groups. Illustrative polyamines included ethylenediamine (EDA) having two amine moieties and tetraethylene pentamine having five amine groups. The second reaction step was carried out in the presence of hypophosphorous acid (and could also include, for example, solid acids such as silica gel, alumina or acid-activated clays, or combinations thereof) and an optional esterification catalyst (preferably at the lower reaction temperatures) at a temperature within the range of from about 150 °C to about 230 °C.

Compounds

The inventive fuel lubricity additives or dispersants can be illustrated according to formula IV.



wherein R₁ is an unsaturated plant oil; wherein R₂ is independently a branched or unbranched, substituted or unsubstituted C₁₋₂₀ alkyl or a C₂₋₂₀ alkenyl group wherein a double bond (if present) is located at least six carbon atoms away from a ring carbon atom and wherein a substitution is selected from the group consisting of hydroxyl, oxo, keto, amino, aminyl, carboxyl, amidinyl, phenyl, and toluenyl; and wherein R₃ is a polyhydroxy third group moiety.

Example 1

This example summarizes the data presented herein. Intermediate products with a number of dienes and dienoids with HEAR oil as the exemplary base oil were synthesized to

form the resultant intermediate product in three molar ratios. The optimum molar ratio was chosen by testing of the viscosity, viscosity index (VI), acid number, iodine number, solubility, 4-ball wear properties. The molar ratios chosen from these tests were HEAR:maleic anhydride @ 1:0.5, HEAR:acrylic acid @ 1:1, and HEAR:sorbic acid @ 1:0.6.

5 The anti-wear properties of the sorbic acid/HEAR were the best of the above-noted intermediate products, improving the polyalphaolefin (PAO) base stock by 30%. All the intermediate products were soluble in the three base stocks up to at least 5%.

The intermediate products were further reacted with polar compounds to produce candidate polyol and polyamine products. The intermediate products were esterified with polyols glycerine (three hydroxyls), and sorbitol (six hydroxyls). They were also reacted with ethylenediamine (EDA) and tetraethylene pentamine (TEPA) to form polyamines. The polyols and polyamines were tested for anti-wear properties. They were evaluated for solubility in base stocks and for emulsibility in water as a condition of detergency.

15 The liquids (polyol esters) and waxes (polyamine amides) that were made were verified by Fourier Transform Infrared (FTIR) Spectrophotometry for chemical structure. All the requisite structures for the expected products were present.

The solubility of the products was altered drastically depending on the polar compound added. Polyamines displayed the lowest solubility problems in all base stocks. The sorbitol esters were the only polyols that had problems dissolving, and then, only, in PAO.

20 A level of 0.2% of the candidate compounds in MVI 100N was emulsified 50:50 with water and allowed to separate. None of the glycerine esters had an effect on the oil/water separation. The sorbitol esters formed stable water-in-oil emulsions and are candidates for a anti-wear dispersant/detergent compound. The polyamine waxes had solubility problems with oil and produced unstable emulsions.

25

Example 2

This provides a summary of nine compositions made showing each of the tree materials, molar ratios and reaction conditions to illustrate the extent and breadth of the invention. The following Table 5 summarizes these reactions and data.

30

Table 5

Base Oil	Adduct	Mol Ratio	Esterification/ Amidification Reactants	Adduction		Product Formation		
				Time Min	Temp C	Cat- alyst	Time Min	Temp C
HEAR	Maleic Anhydride	1:0.5	Glycerol	240	120	HPA*	240	160
HEAR	Maleic Anhydride	1:0.5	Sorbitol	240	120	HPA*	240	160
HEAR	Maleic Anhydride	1:0.5	Hydroquinone	240	120	HPA*	300	190

HEAR	Maleic Anhydride	1:0.5	Ethylene diamine	240	120		120	120
HEAR	Acrylic Acid	1:1	Sorbitol	360	170	HPA*	240	160
HEAR	Sorbic Acid	1:1	Ethylene diamine	360	200		120	120
HEAR	Sorbic Acid	1:1	Tetraethylene penatmine	360	200		120	120
HEAR	Acrylic Acid	1:1	Hydroquinone	360	170	HPA*	300	190
HEAR	Sorbic Acid	1:1	Hydroquinone	360	200	HPA*	300	190
SOY	Sorbic Acid	1:1	Sorbitol	360	200	HPA*	240	160

*HPA=Hypophosphorus Acid

Example 3

This provides a summary of data evaluating various diesel fuel lubricity additives for lubricity, fuel properties, combustion and deposits. Lubricity was measured using an industry standard Scuffing Load Ball on Cylinder (SLBOCLE), ASTM D-6078, and High Frequency Reciprocating Rig (HFRR), ASTM D-6079 tests. The data compare no lubricity additive with three different concentrations of inventive lubricity additive SSS-1.7.7, which is a soy oil-sorbic acid-sorbitol product at 1:1 molar ratios. The data are provided in Table 6.

Table 6

FUEL OIL GRADE	TEST	PASSING VALUE	NO ADD-ITIVE	SSS-1.7.7		
				2000 ppm	500 ppm	100 ppm
#1 Diesel Fuel (kerosene)	SLBOCLE	>3100	1250	5350	3650	2250
	HFRR	<450	675	176	303	656
Source A #2 Diesel Fuel	SLBOCLE	>3100	4200	NT	5050	4100
	HFRR	<450	531	NT	261	500
Source T #2 Diesel Fuel	SLBOCLE	>3100	4000	NT	5400	4875
	HFRR	<450	502	NT	178	222

NT denotes Not Tested

In addition, the fuel properties of a diesel fuel containing 500 ppm of the inventive SSS-1.7.7 fuel lubricity additive showed that the fuel properties were not affected by addition of 500 ppm of the inventive fuel lubricity additive.

Table 7

TEST	REFERENCE	500 ppm SSS 1.7.7 ADDED
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Cetane Number	47.2	47.8
Cold Filter Plugging Point ASTM D	-20 C	-20 C

- 5 An emissions and combustion test was conducted on a 276 CID, John Deere 4276T turbocharged, direct-injected, 4 cylinder diesel engine mounted on a dynamometer. The engine speed and torque output were varied in three sections during the 125 hour test. Any problems with combustion or injector deposits show up as high final values of Hydrocarbons and Carbon Monoxide (CO) and smoke (BSN) in the exhaust. The diesel fuel used had 500 ppm of SSS-1.7.7 added. The data provided in Table 8 show that the fuel with additive did not affect any change in engine operation.

Table 8

TEST CONDITIONS	EMISSIONS	INITIAL	FINAL
<i>Section 1-Peak Torque</i>	CO, ppm	129	101
1400 RPM	CO ₂ , %	8.0	8.3
220 ft-lb Torque	Hydrocarbons, ppm C ₆	32.6	31.6
	Smoke (BSN)	1.77	1.83
<i>Section 2-Rated Power</i>	CO, ppm	95	85
2100 RPM	CO ₂ , %	7.5	7.3
187 ft-lb Torque	Hydrocarbons, ppm C ₆	27.9	24.8
	Smoke (BSN)	0.67	0.73
<i>Section 3-Light Load</i>	CO, ppm	252	268
1200 RPM	CO ₂ , %	2.9	2.1
30 ft-lb Torque	Hydrocarbons, ppm C ₆	55.9	51.2
	Smoke (BSN)	0.63	0.60

- 10 The values are within experimental error for each of the initial and final readings, indicating little or no change in the engine operation.

- 15 A Cummins L-10 deposits test was run with a Cummins 6 cylinder diesel engine in accordance with Cummins Test Method 60032. The fuel used was Howell 0.4% (4000 ppm) Sulfur fuel, the only reference fuel available for the method. (Cummins has not chosen a low-sulfur reference fuel as of this study.) The results of the Cummins L-10 deposit test in Table 9 show that the inventive diesel fuel lubricity additive did not affect the deposit characteristics of the fuel to any significant degree.

Table 9

TEST PARAMETER	REFERENCE FUEL	REFERENCE FUEL PLUS
Change at End of Test		250 PPM SSS-1.7.7

Average Flow Rate Loss	6.0% Maximum	5.8%
Average CRC Rating of 6 Injectors	21.2 - 28.6 Range	23.6

We claim:

1. A fuel lubricity additive compound, comprising an intermediate adduct of a first moiety reacted in a first reaction with a second moiety to form the intermediate adduct and further esterifying or amidifying the intermediate adduct with a third moiety in a molar ratio of from about 1:2 to about 2:1, wherein the first moiety is a unsaturated triglyceride plant oil or a thermal polymer thereof, wherein the second moiety is a diene or conjugated double bond acid or anhydride moiety, wherein the first reaction comprises mixing the first moiety with the second moiety in a molar ratio of from about 1:2 to about 2:1 at a temperature of from about 130 °C to about 195 °C under an inert atmosphere; and wherein the third moiety is a polyhydroxy compound or a polyamino compound.
2. The fuel lubricity additive of claim 1 wherein the unsaturated plant oil is selected from the group consisting of rapeseed oil, tung oil, linseed oil, soya oil, corn oil, peanut oil, canola oil, safflower oil, or combinations thereof.
3. The fuel lubricity additive of claim 1 wherein the thermal polymer is selected from the group consisting of thermal (telomer) polymers of canola oil, soya oil, linseed oil, corn oil, safflower oil, peanut oil, tung oil, and combinations thereof.
4. The fuel lubricity additive of claim 1 wherein the second moiety comprises unsaturated compounds having a free carboxylic acid or anhydride group.
5. The fuel lubricity additive of claim 4 wherein the second moiety is selected from the group consisting of maleic acid, maleic anhydride, sorbic acid, sorbic anhydride, tetrahydrophthalic anhydride, tetrahydrophthalic acid, salicylic acid, salicylic anhydride, acrylic acid, acrylic anhydride, C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, or C₁₋₁₀ alkoxy derivatives of the foregoing acids and anhydrides, and combinations thereof.
6. The fuel lubricity additive of claim 1 wherein the polyhydroxy compound of the third moiety is selected from the group consisting of glycerol, sorbitol, hydroxyquinone, glucose, mannose, 6-carbon sugars, pentose, fructose, 5-carbon sugars, pentaerythritol, catechol, resorcinol, hydroquinone, pyrogallol, 4,4'-dihydroxybiphenyl, 2,4-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, orthohydroxybenzene, polyhydroxyaromatic compounds having one or two phenyl rings and one or two 5-6 membered aromatic rings having substituted alkyl or alkenyl side chains (C₂₋₁₀) substituted with at least two hydroxyl groups, trimethylolpropane, pentaerythritol, dimethylolpropane, dipentaerythritol, trimethylolethane, ethyleneglycol, polypropyleneglycol, polyethylated alcohols, and combinations thereof.
7. The fuel lubricity additive of claim 1 wherein the polyamino compound is selected from the group consisting of diethylenetriamine, dimethylenetriamine, dipropylenetriamine, ethylenediamine, propylenediamine, butylenediamine, butylenetriamine, triethylenetetramine, tripropylenetetramine, trimethylenetriamine, tributylenetetramine, tetraethylenepentamine, tetramethylenepentamine, tetrapropylenepentamine, tetrabutylenepentamine, hexylenediamine, and combinations thereof.

8. The fuel lubricity additive of claim 1 wherein the first reaction is conducted under continuous mixing.

9. The fuel lubricity additive of claim 1 wherein the esterification reaction comprises reaction conditions of from about 150 °C to about 190 °C under an inert atmosphere and further comprises adding an esterification catalyst.

10. The fuel lubricity additive of claim 9 wherein the esterification catalyst is an acid catalyst.

11. The fuel lubricity additive of claim 10 wherein the esterification catalyst is selected from the group consisting of p-toluene sulfonic acid, hydrophosphorous acid, sulfuric acid, hydrochloric acid, phosphoric acid, acid-activated clays, solid acid catalysts, acidic zeolites, and combinations thereof.

12. The fuel lubricity additive of claim 1 wherein the amidification reaction comprises reaction conditions of from about 130 °C to about 150 °C under an inert atmosphere.

13. The fuel lubricity additive of claim 1 wherein the fuel lubricity additive compound is made from the first moiety, second moiety and third moiety compounds selected from the group consisting of in order soya oil-maleic anhydride-sorbitol, soya oil-linseed oil combination-maleic anhydride-sorbitol, soya oil-maleic anhydride-ethylenediamine, and soya oil-maleic anhydride-hydroquinone.

14. A process for synthesizing a fuel lubricity additive compound, comprising
(a) reacting an unsaturated triglyceride plant oil or a thermal polymer thereof first moiety with a second moiety in a molar ratio of from about 1:2 to about 2:1 at a temperature of from about 130 °C to about 195 °C under an inert atmosphere to form an intermediate adduct, wherein the second moiety is a diene or conjugated double bond acid or anhydride moiety; and
(b) esterifying or amidifying the intermediate adduct with a third moiety in a molar ratio of from about 1:2 to about 2:1, wherein the third moiety is a polyhydroxy compound or a polyamino compound.

15. The process of claim 14 wherein the unsaturated plant oil is selected from the group consisting of rapeseed oil, tung oil, linseed oil, soya oil, corn oil, peanut oil, canola oil, safflower oil, or combinations thereof.

16. The process of claim 14 wherein the thermal polymer is selected from the group consisting of thermal (telomer) polymers of canola oil, soya oil, linseed oil, corn oil, safflower oil, peanut oil, tung oil, and combinations thereof.

17. The process of claim 14 wherein the second moiety comprises unsaturated compounds having a free carboxylic acid or anhydride group.

18. The process of claim 17 wherein the second moiety is selected from the group consisting of maleic acid, maleic anhydride, sorbic acid, sorbic anhydride, tetrahydrophthalic anhydride, tetrahydrophthalic acid, salicylic acid, salicylic anhydride, acrylic acid, acrylic anhydride, C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, or C₁₋₁₀ alkoxy derivatives of the foregoing acids and

anhydrides, and combinations thereof.

19. The process of claim 14 wherein the polyhydroxy compound of the third moiety is selected from the group consisting of glycerol, sorbitol, hydroxyquinone, glucose, mannose, 6-carbon sugars, pentose, fructose, 5-carbon sugars, pentaerythritol, catechol, resorcinol, hydroquinone, pyrogallol, 4,4'-dihydroxybiphenyl, 2,4-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, orthohydroxybenzene, polyhydroxyaromatic compounds having one or two phenyl rings and one or two 5-6 membered aromatic rings having substituted alkyl or alkenyl side chains (C₂₋₁₀) substituted with at least two hydroxyl groups, trimethylolpropane, pentaerythritol, dimethylolpropane, dipentaerythritol, trimethylolethane, ethyleneglycol, polypropyleneglycol, polyethylated alcohols, and combinations thereof.

20. The process of claim 14 wherein the polyamino compound is selected from the group consisting of diethylenetriamine, dimethylenetriamine, dipropylnetriamine, ethylenediamine, propylenediamine, butylenediamine, butylenetriamine, triethylenetetramine, tripropylenetetramine, trimethylenetriamine, tributylenetetramine, tetraethylenepentamine, tetramethylenepentamine, tetrapropylenepentamine, tetraethylenepentamine, tetrabutylenepentamine, hexylenediamine, and combinations thereof.

21. The process of claim 14 wherein the first reaction is conducted under continuous mixing.

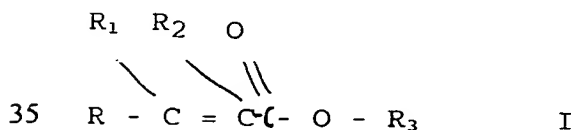
22. The process of claim 14 wherein the esterification reaction comprises reaction conditions of from about 150 °C to about 190 °C under an inert atmosphere and further comprises adding an esterification catalyst.

23. The process of claim 14 wherein the esterification catalyst is an acid catalyst.

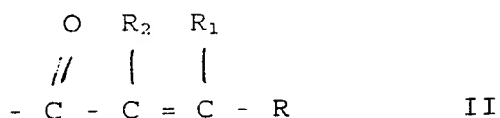
24. The process of claim 23 wherein the esterification catalyst is selected from the group consisting of p-toluene sulfonic acid, hydrophosphorous acid, sulfuric acid, hydrochloric acid, phosphoric acid, acid-activated clays, solid acid catalysts, acidic zeolites, and combinations thereof.

25. The process of claim 14 wherein the amidification reaction comprises reaction conditions of from about 130 °C to about 150 °C under an inert atmosphere.

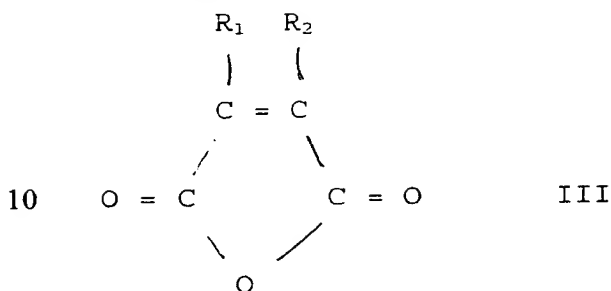
26. A fuel lubricity additive or a dispersant comprising a product of a first and a second reaction, (a) wherein the first reaction is an addition reaction of a base oil and a dienophile having a carboxylic acid moiety selected from a formula I or a formula III:



wherein R, R₁ and R₂ are independently hydrogen, hydroxyl, a straight chain or branched chain C₁₋₁₂ alkyl, C₁₋₁₂ acyl, C₁₋₁₂ aryl, C₄₋₁₂ cycloalkyl, or C₁₋₁₂ alkoxy; and wherein R₃ is hydrogen, a straight chain or branched chain C₁₋₁₂ alkyl, C₁₋₁₂ acyl, C₁₋₁₂ aryl, C₄₋₁₂ cycloalkyl, or C₁₋₁₂ alkoxy, or formula II



5 or formula III



wherein R_1 and R_2 are the same as in formula I; and

- (b) wherein the second reaction is an esterifying or an amidafying of the carboxylic acid functional moiety of the aliphatic intermediate product of the first reaction with a polyol compound or polyamino compound having from 2 to 10 free hydroxyl groups and selected from the group consisting of substituted or unsubstituted mono-, di-, tri-, tetra- or penta-sugars, glycerols, glycols, pentaerythrols, and combinations thereof, wherein the substitutions are selected from the group consisting of hydroxyl, oxo, halogen (chloro, bromo, iodo, fluoro), straight chain or branched chain C_{1-12} alkyl, C_{1-12} acyl, C_{1-12} aryl, C_{4-12} cycloalkyl, hydroxyl, and C_{1-12} alkoxy.

27. The fuel lubricity additive of claim 26, wherein the dienoid carboxylic acid is selected from the group consisting of maleic acid, phthalic acid, sorbic acid, acrylic acid, and combinations thereof.

28. The fuel lubricity additive of claim 26, wherein the base oil is selected from the group consisting of HEAR (high erucic acid rapeseed oil), linseed oil, soybean oil, canola oil, telomer oil having a kinematic viscosity of 6000 SUS, and combinations thereof.

29. The fuel lubricity additive of claim 26, wherein the base oil is either a triglyceride (all straight chain) with at least one of the acyl chains being unsaturated, or a straight chain wax ester of from about 18-48 carbons atoms in length and being at least monounsaturated.

30. The fuel lubricity additive of claim 29, wherein the base oil acyl fatty acid chains of the triglyceride are from 3 to 24 carbon atoms in length (straight) and have from one to three double bonds.

31. The fuel lubricity additive of claim 30, wherein the base oil unsaturated fatty acid acyl chains have from 10-24 carbons atoms.

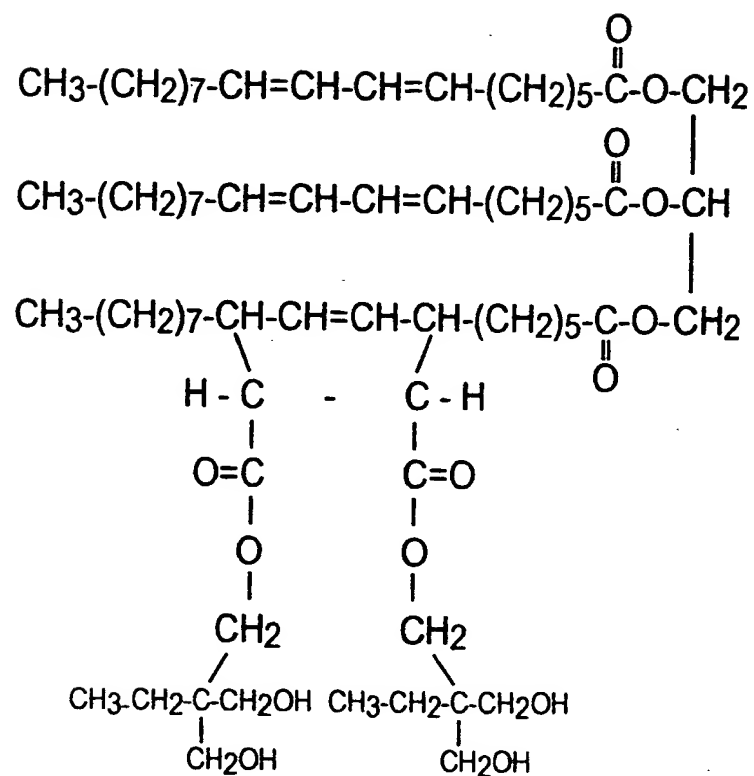
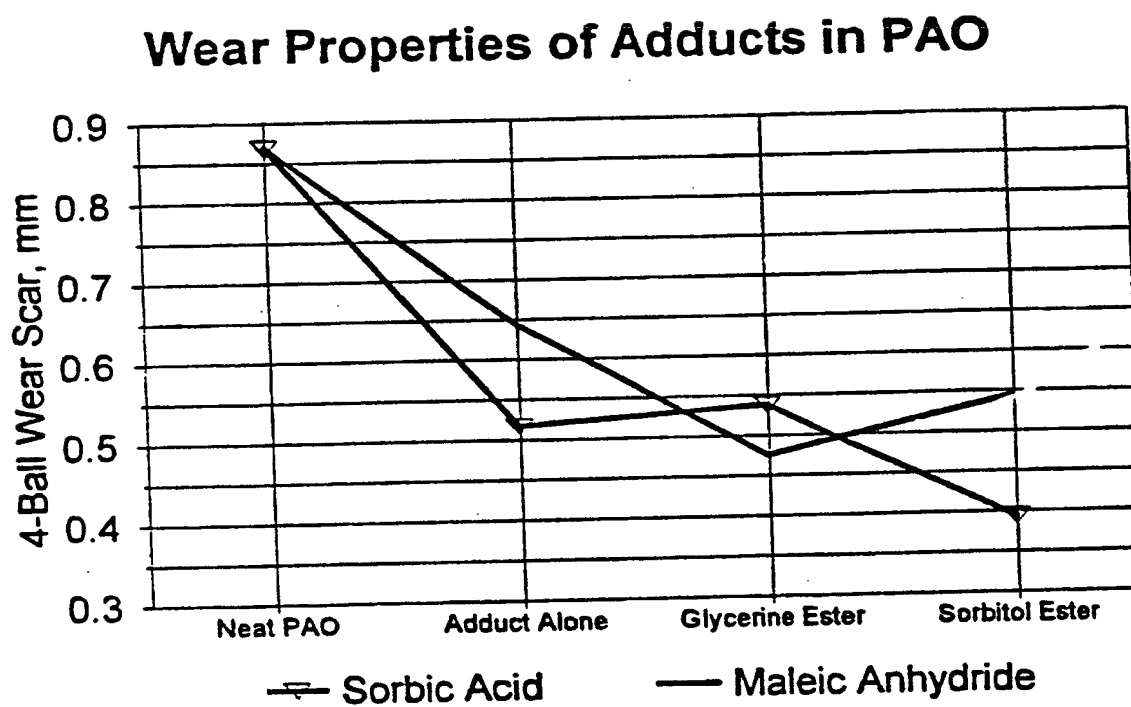
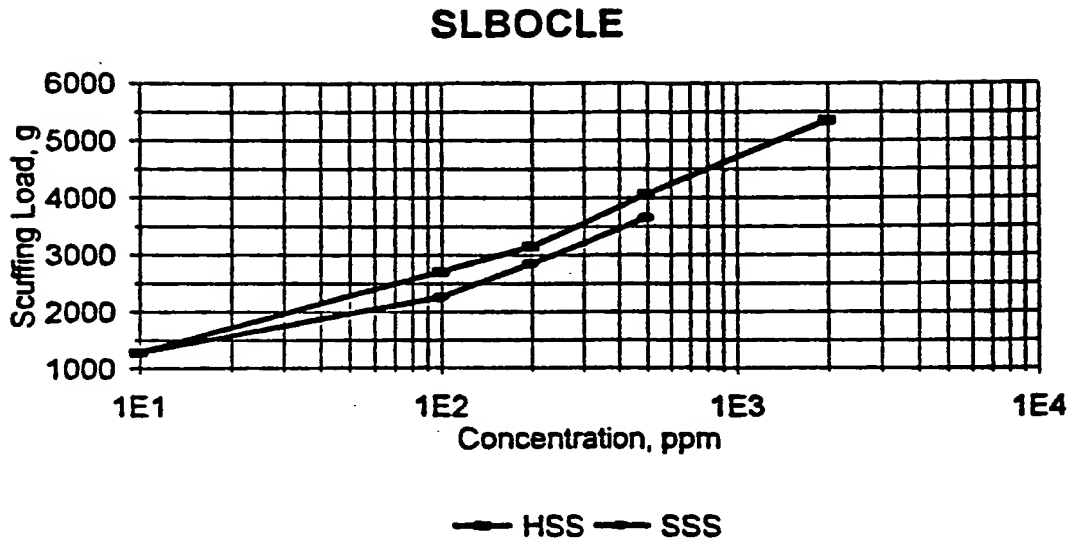
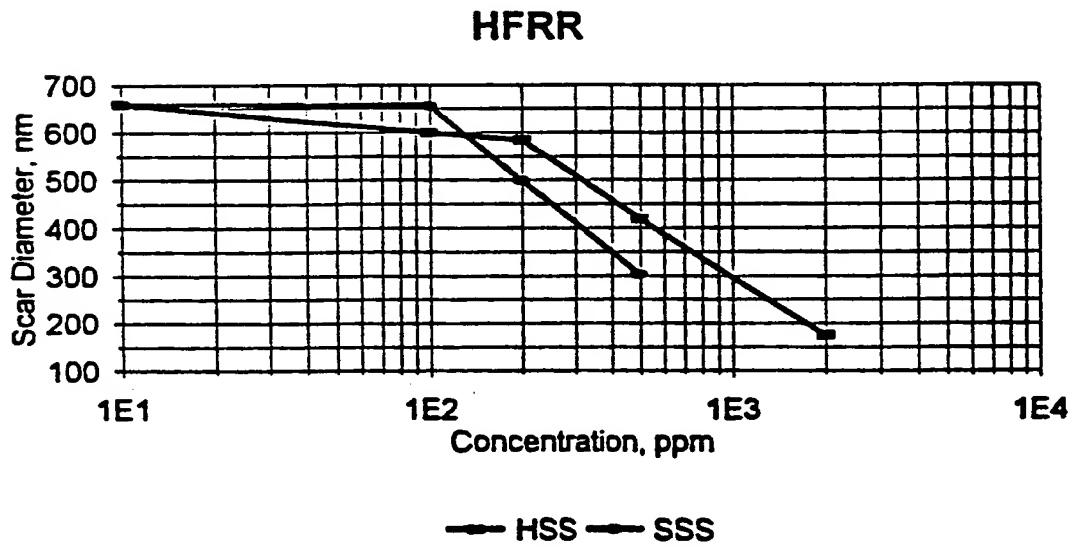


Fig. 1

**Fig. 2**

**Fig. 3A****Fig. 3B**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/11627

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18; C07C 59/00
US CL : 44/385, 388, 389, 403, 404; 554/117
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/385, 388, 389, 403, 404; 554/117

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS, CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5,833,722 A (DAVIES et al.) 10 November 1998, entire document.	1-31
A,P	US 5,858,028 A (DAVIES et al.) 12 January 1999, entire document.	1-31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
26 AUGUST 1999

Date of mailing of the international search report
15 October 1999 (15.10.99)

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